SLURRY REACTOR HYDRODYNAMIC STUDIES

Executive Summary

Air Products, under U.S. Department of Energy Contract No. DE-AC22-80PC30021, has developed new slurry catalyst compositions and slurry phase bubble column reactor correlations for the Fischer-Tropsch (FT) synthesis. This report presents results of the cold-flow slurry reactor hydrodynamic studies (Contract Task 3).

The objective of the slurry reactor modeling studies was to evaluate, through the use of cold flow simulators, the hydrodynamics, flow characteristics, and behavior of slurry reactors for the production of hydrocarbons from synthesis gas.

The slurry reactor modelling consisted of three major phases. In the first phase hydrodynamic information was obtained in a 5" ID x 5' (12.7 cm ID x 1.52 m) cold flow simulator. In the second phase of the project, the first hydrodynamic study was scaled up in a 12" ID x 15.5' (30.5 cm ID x 4.75 m) column. Also, some additional dependent variables were studied. Finally, in the third phase, kinetic data obtained from the catalyst studies in Task 2, along with the hydrodynamic correlations obtained in the first two phases of Task 3, were incorporated into a computer model. This computer model was used to predict the conversion rates and space-time yields, or production rates/unit volume, to be obtained in actual FT slurry reactor operation. From the model the heat, mass, and momentum transfer parameters, which most affect the bubble column design, were better quantified.

The major results of the study are summarized as follows:

- For the systems studied, both hydrodynamic and kinetic effects are important to the proper design of the bubble column reactor.

- With solid particles below 60 µm, the slurry can be modelled as a pseudo-single phase.

- Larger size solid particles, 100 µm, were found to distribute themselves in accordance with Cova's (1967) sedimentation-diffusion model.

- The most important independent variable studied affecting column performance was superficial gas velocity. The next most important parameter was solid particle loading. The liquid type had a small effect on column hydrodynamics. Those parameters that had little or no effect on column hydrodynamics in the range studied included the presence of heat transfer internals, solid type, distributor hole size, and superficial slurry velocity.

- Staging the bubble column system to provide more plug flow behavior is predicted to result in a 5% increase in conversion rates, assuming the same bubble size, about 0.23 cm, as in the unstaged column. A 25% increase in conversion rates is predicted assuming a 0.07 cm average diameter bubble.

- Gas holdup, in the cold flow systems studied, was lower than that measured by Deckwer (1981) and Mobil (Kuo, 1983) using a 5 cm reaction vessel, but in agreement with results of Satterfield (1980) and with correlations from Air Products' slurry phase methanol project (Dyer, 1984).

- While this lower predicted gas holdup had a desirable effect on reactor products and on rates, it cannot be asserted that any of the above correlations can accurately predict gas holdup in a commercial-size slurry Fischer-Tropsch reactor.

- Adding seven, 5.7 cm O.D. x 1.42 m heat transfer internals to the 30.5 cm column had no effect on column hydrodynamics.

- The heat transfer results agreed with Deckwer's correlation (1980b); however, contrary to Deckwer's results, the heat transfer rates continued to increase beyond a 10 cm/s superficial gas velocity.

- Accordingly, heat transfer internals would be expected to take up only a small faction of the available bubble column cross section making the use of heat transfer cooling, internal to an FT reactor, an attractive mode of operation.

- Mass transfer results agreed with Akita and Yoshida (1973) and Hikita et al. (1973).

- Liquid dispersion results agreed with Kato et al. (1972b), indicating that above a superficial gas velocity of 3 cm/s, the slurry was well-mixed.

This detailed report provides experimental procedures, data, correlations, and mathematical derivations to quantify, for the systems studied, the above results. While the data obtained in this program has reduced the uncertainty of designing an FT bubble column reactor, it was never intended to eliminate the need for operating an actual Fischer-Tropsch bench scale facility. Recognizing the inherent limitation of a cold flow study, the computer model was used to design a bench scale facility slurry Fischer-Tropsch reactor. That design is reported under separate cover.

1.0 INTRODUCTION

Coal liquefaction will be an important source of transportation fuels in the future and can be accomplished by either a direct route (hydrogenation of coal in a donor solvent) or an indirect route (gasification of coal followed by the Fischer-Tropsch reaction).

The product selectivity of the Fischer-Tropsch reaction has been the focus of extensive research for many years, yet still remains a prime target for technical innovation. Fischer-Tropsch technology, as it is currently practiced commercially for liquid fuels production, provides a broad range of hydrocarbon products which require costly downstream processing.

Selectivity can be influenced by variations in the catalyst composition and process conditions. Yet, in spite of the extensive effort devoted to this problem, a suitable catalyst has not yet been developed for producing a narrow boiling range hydrocarbon product, such as gasoline or diesel fuel, without the coproduction of undesirable lighter and heavier products.

The Fischer-Tropsch reaction is exothermic, and improved heat transfer would also be expected to have a major beneficial effect on product selectivity. Slurry phase reactor operation improves heat transfer and temperature control and results in greater selectivity to liquid products, usually through lower methane production. However, considerable differences have been reported in the space-time yield, catalyst life, and ease of operation of slurry phase reactors.

In addition to improved product selectivity, slurry phase operation offers the advantage of ease of scale-up and the ability to directly utilize the carbon monoxide-rich synthesis gas produced by modern coal gasifiers. The full potential of the slurry phase Fischer-Tropsch process has not yet been realized, and its further development is an important factor for establishing viable technology to convert coal to hydrocarbon liquid fuels.

Air Products, under DOE Contract DE-AC22-80PC30021, has undertaken a program in catalyst and reactor development for a slurry phase Fischer-Tropsch process. This report describes the cold-flow hydrodynamic correlations developed in Task 3 of that contract.

1.1 Background

Most of the Fischer-Tropsch work documented in the literature focuses on gas phase, fixed bed, and fluidized bed processes. This is not surprising since all of the commercial Fischer-Tropsch plants have utilized gas phase processes.

In 1936, German researchers began to develop a liquid phase Fischer-Tropsch process. Development work continued, with some interruptions, until the mid-1950s. Although a commercial liquid phase plant was never built because of declining interest in Fischer-Tropsch technology during the late 1950s, a demonstration plant was constructed and operated at Rheinpreussen.

A major advantage of the liquid phase process was improved selectivity, achieved mainly by a drastic reduction in methane formation (Kolbel and Ackerman, 1951; Kolbel et al, 1955). This is generally attributed to better temperature control at the catalyst surface.

Between 1944 and 1955, the U.S. Bureau of Mines (1959) conducted research on a liquid phase Fischer-Tropsch process in their synthetic liquid fuels program. This work also demonstrated the improved selectivity of the liquid phase process for gasoline and diesel fuel products.

Hall and coworkers (1952) at the British Fuel Research Station compared the fixed bed, liquid phase, and fluidized bed processes. Like the other investigators, they also reported improved selectivity with the liquid phase process.

In addition to reduced methane formation, the liquid phase process offers the important advantage of encouraging the Kolbel-Engelhardt reaction, i.e., the direct conversion of carbon monoxide and steam to hydrocarbons. The ability to operate within a wide range of synthesis gas compositions (Kolbel and Ackerman, 1951), even including wet blast furnace gas (34% CO, 2% H_2, 7% CO_2, 57% N_2; dry basis) (Kolbel et al., 1955), eliminates the separate shift conversion of the carbon monoxide-rich product from a coal gasifier. Thus the liquid phase FT process using a slurry reactor holds promise as being a more economical route to transportation fuels.

1.2 Slurry Reactors

A slurry reactor is any gas-liquid-solid contactor where the solid and liquid tend to move together and a chemical reaction takes place. Ramachandran and Chaudhari (1980) describe the various types of slurry reactors (Figure 1.2). In this report, however, a slurry reactor will mean only the bubble column slurry reactor, a hollow cylindrical vessel with gas sparged at the bottom and slurry either flowing cocurrently (continuous mode) or sitting stationary (batch mode). A bubble column will be assumed to be three-phase unless otherwise noted. In the literature, this device is also called an entrained bed reactor.

The advantages of slurry reactors over fixed bed and solid-gas, fluidized bed reactors for the Fischer-Tropsch synthesis have been described by Kolbel (1951, 1980) and Hall et al. (1952). These advantages include:

- Higher selectivity to C_5+ products, owing to the prevention of local catalyst particle overheating and consequent excessive methane production.

- Ability to use carbon monoxide-rich synthesis gas without plugging the reactor or fouling the catalyst particles by carbon formation.

- Increased flexibility in choice of operating conditions (temperature, pressure, and catalyst type) to maximize yields of products of the desired molecular weight range.
- High conversion of synthesis gas in a single pass.
- Uniform utilization of catalyst due to slurry phase backmixing.
- Ease of catalyst replacement without interrupting the operation.
- Ease of scale-up to commercial size.

1.3 Flow Regimes

With the liquid as the continuous phase, the gas flow pattern can be categorized as shown by Deckwer (1980) as bubbly flow, slug flow, or churn-turbulent flow. As each flow pattern exhibits different hydrodynamic behavior, it is helpful to analyze each flow pattern separately. Taitel, Bornea, and Dukler (1980) and Weismann and Kang (1981) have attempted to predict which flow pattern would be present in a vertical tube based on fluid velocities, fluid properties, and pipe size. The gas flow pattern is determined primarily by the competing rates of bubble coalescence and breakup, which in turn depend on liquid phase properties such as viscosity, surface tension, and density.

Bubble coalescence involves the processes of drawing bubbles together with concomitant rupture of the thin film of liquid separating the bubbles. Gas bubbles apparently coalesce by the capture of one bubble in the wake of another rising bubble; this has been extensively studied by Crabtree and Bridgwater (1971). Sagert and Quinn (1978) showed that film thinning, and thus bubble coalescence, in low viscosity systems is reduced as solute diffusion to the film surface is reduced. Calderbank et al. (1965) reported that increasing liquid viscosity enhances the rate of bubble coalescence.

Bubble breakup is due to disturbance at the interface. In the early fifties, Davies and Taylor (1950) performed a theoretical study on the instability of liquid surfaces. This mechanism was later proposed by Clift and Grace (1972) to explain bubble breakup.

One of the more important aspects of gas flowing through a tubular reactor is its availability at the reaction site. This is ultimately related to the interfacial area between the liquid and gaseous phases. In a two-phase, gas-liquid system, the interfacial area, a, is related to the gas volume fraction, ε_G, and mean bubble size, d_{SB}, by

$$a = 6\ \varepsilon_G / d_{SB} \tag{1.3.1}$$

Both the mean bubble size, also known as the Sauter mean diameter, and the volume fraction, which is typically referred to as gas holdup or void fraction, are values which are extremely important to optimum reactor design.

2.0 Task 3 Objective

The objective of the slurry reactor modeling studies was to evaluate, through the use of cold flow simulators, the hydrodynamics, flow characteristics, and behavior of slurry reactors for the production of hydrocarbons from synthesis gas.

The slurry reactor modelling consisted of three major phases. In the first phase hydrodynamic information was obtained in a 5" ID x 5' (12.7 cm ID x 1.52 m) cold flow simulator. In the second phase of the project, the first hydrodynamic study was scaled up in a 12" ID x 15.5' (30.5 cm ID x 4.75 m) column. Also, some additional dependent variables were studied. Finally, in the third phase, kinetic data obtained from the catalyst studies in Task 2, along with the hydrodynamic correlations obtained in the first two phases of Task 3, were incorporated into a computer model. This computer model was used to predict the conversion rates and space-time yields, or production rates/unit volume, to be obtained in actual FT slurry reactor operation. From the model, the heat, mass and momentum transfer parameters, which most affect the bubble column design, were better quantified.

2.1 Dependent Variables

One potential limitation on the application of slurry reactors is the conversion capacity per unit volume of slurry.

There is some disagreement in the literature on whether the production rates in an FT slurry reactor are limited by mass transfer resistance, i.e., the rate at which reacting gas can transfer into the liquid phase, or kinetic resistance, i.e., the kinetic reaction rate of the catalyst. Gas holdup, or the gas volume fraction in the column, average bubble size, and mass transfer coefficient all affect the degree to which the overall reaction is limited by mass transfer of reactants. If gas-liquid mass transfer limitations are controlling, then these would be the only parameters needing study. Two parameters, solids dispersion and liquid dispersion, affect the maximum catalyst loading and are important for the kinetic controlled regime. The heat transfer coefficient determines how much heat transfer surface is required inside the reactor, which directly affects how much volume remains for the reaction. It is anticipated in the optimum bubble column design that mass and kinetic resistances, and possibly heat transfer resistances, may be controlling. Thus, it was necessary to quantify all of the above-mentioned parameters.

Included in Table 2.1 is a list of the hydrodynamic parameters, or dependent variables, that were investigated in the first two phases of the slurry reactor modeling program. These variables were studied because substantial differences in reactor performance, and thus plant costs, were obtained using existing literature correlations. By obtaining experimental data on these parameters, uncertainty in the optimum reactor design was considerably reduced.

The factors which were studied in this task include:

- Gas holdup, or the volume fraction of gas in the reactor,
- Mass transfer from the gas to the liquid phase,
- Interfacial area between the gas and liquid,
- Bubble size,
- Heat transfer from the slurry to internal cooling surfaces (if employed),
- Catalyst dispersion along the reactor height, and
- Liquid dispersion.

2.2 Independent Variables

The independent variables, shown in Table 2.1, were chosen to amply bracket the range of conditions anticipated in a slurry phase FT process. The operating conditions used for the Rheinpreussen slurry phase FT pilot plant (Kolbel & Ralek, 1980) were considered typical. In that work, a 20 wt % slurry, 50 µm average particle size, of precipitated iron oxide catalyst was used. The gas operated from 6.1 to 9.1 cm/sec superficial velocity. With heat transfer internals, circulation of slurry to an external cooler was unnecessary. However, as it was unknown whether internal or external cooling would be optimal in this work, a sufficiently high slurry velocity was studied in the 12.7 cm column to allow only a 10°C temperature rise of the slurry in the reactor in the event that external cooling was used.

Various perforated plate gas distributor hole sizes were investigated. Perforated plates were chosen because distributor plate fouling did not appear to be a problem at Rheinpreussen.

The two liquids used were water and isoparaffin, a C_9-C_{11} branched hydrocarbon. Water was chosen to relate the bulk of the literature data to this study. Isoparaffin was chosen to simulate the Rheinpreussen paraffinic-type oil.

3.0 Experimental Procedure

Experiments were conducted in 12.7 cm ID x 1.52 m Plexiglas and 30.5 cm ID x 475 cm borosilicate glass columns (see Figure 3.1). Four ports to sample the solid concentration were mounted at approximately 9, 38, 76 and 114 cm above the perforated plate distributor in the 12.7 cm column, and 2, 15, 302, and 453 cm in the 30.5 cm column.

Table 2.1 shows the size ranges and concentrations of the slurries of silicon and iron oxides in isoparaffin (Soltrol 100, see ref.) and water that were utilized in the tests. From the stirred, baffled reservoir tank, which was approximately the same volume as the columns, slurry was pumped with a diaphragm pump, using a tranquilizer to even out the flow, into the bottom of the 12.7 cm column, and above the distributor for the 30.5 cm column. In the 12.7 cm column, therefore, slurry passed with the gas through the distributor plate for $j_L > 0$. At the top of the column, the slurry was separated from the gas, and returned by gravity either to the reservoir tank or to a calibrated volume used for slurry flow measurement.

Nitrogen or air was metered with a rotameter in the 12.7 cm column, and with a differential pressure cell in the 30.5 cm column, and entered the columns beneath the distributor plate.

With the highest slurry loadings, a small gas sidestream was also used in the slurry feed to facilitate pumping from the reservoir to the column.

For the 12.7 cm column, the gas and slurry distributor was 1.25 mm thick, with a 10% to 13% open area of 0.9 mm holes. The 30.5 cm column used different 0.3% open area distributor plates, with 0.9, 3.2 and 12.8 mm diameter holes. The gas traveled with the slurry, separated at the column top, and passed through a demister pad, liquid trap, and rotameter before being vented. All metal parts were grounded to prevent electric arcing during experiments with the nonconducting hydrocarbon liquid.

4.0 Physical Property Determination

Liquid and solid physical property values are listed in Table 4.0. The temperature dependence of the physical properties for water and the two oxides was obtained from the literature (Washburn, 1926; Mellor, 1937). Density, viscosity, and surface tension measurements of the isoparaffin, a C_9-C_{11} branched isomer mixture, were made. The measured values of viscosity and surface tension were in close agreement to the estimated properties of a 72 vol% n-C_{11}/28% n-C_{12} mixture using the Chao-Seader method (1961). Therefore heat capacity and thermal conductivity values calculated for this mixture were used for the isoparaffin.

Slurry properties were determined using the following relationships (terms defined in Section 13.0):

$$C_{PSL} = w_S C_{PS} + w_L C_{PL} \qquad (4.0.1)$$

$$k_{SL} = \frac{2k_L + k_S - 2v_S(k_L - k_S)}{2k_L + k_S + v_S(k_L - k_S)} k_L \quad \text{(Tareef, 1940)} \qquad (4.0.2)$$

$$\rho_{SL} = v_S\rho_S + v_L\rho_L \qquad (4.0.3)$$

The slurry viscosity determination was more complex. As these systems showed dilatant behavior, it was necessary to know the shear rate in the bubble column. Slurry viscosity was measured for 30 wt%, 1-5 μm, silicon oxide and 90-106 μm silicon and iron oxides in isoparaffin slurries as a function of shear rate by Tekmar using a Contraves rheostat viscometer. The results were correlated by:

$$\mu_{SL} = 0.0025\ \gamma^{0.582} \quad \text{(1-5 μm silicon oxide)} \qquad (4.0.4)$$

$$\mu_{SL} = 0.0014\ \gamma^{0.533} \quad \text{(both 90-106 μm slurries)} \qquad (4.0.5)$$

It was unexpected that the silicon and iron oxides gave identical shear rate curves.

The bubble column shear rate, γ, was obtained from the Nishikawa, Kato and Hashimoto (1977) relation,

$$\gamma = 50.0\ V_G \qquad \text{for } V_G < 4.0 \text{ cm/s} \qquad (4.0.6)$$

$$\gamma = 100\ V_G^{\ 0.5} \qquad \text{for } V_G > 4.0 \text{ cm/s} \qquad (4.0.7)$$

The volume fraction at which the slurry viscosity approaches infinity was determined by the Sikdar and Ore (1979) relation,

$$v_\infty = v_{SL}\mu_{SL}/(\mu_{SL}-\mu_L) \qquad (4.0.8)$$

Viscosities at other weight loadings were determined by rearranging equation (4.0.8),

$$\mu_{SL} = \mu_L(v\infty/(v\infty-v_{SL})) \qquad (4.0.9)$$

The 90-106 μm iron and silicon oxides gave identical viscosity vs. shear rate values. It was assumed that other iron and silicon oxide slurries with particle sizes similar to each other would likewise yield identical viscosity vs. shear rate results. Viscosities for the 45–53 μm oxides were interpolated from the 1-5 and 90–106 μm data.

5.0 Gas Holdup

5.1 Literature Review

Gas holdup has been examined by numerous investigators, in both two and three phase systems.

5.1.1 Gas-Liquid Systems

To focus attention on the relative motion of the phases, Wallis (1969) defined the drift-flux as

$$j_{GL} = U_{GL}*\varepsilon_G*(1-\varepsilon_G) = j_G - (j_L+j_G)*\varepsilon_G \qquad (5.1.1.1)$$

It was suggested by Lapidus and Elgin (1957) that the relative (slip) velocity,

$$U_{GL} = j_G/\varepsilon_G - j_L/(1-\varepsilon_G), \qquad (5.1.1.2)$$

is some function of the terminal single bubble rise velocity, u_B,

$$U_{GL} = u_B*f(\varepsilon_G) \qquad (5.1.1.3)$$

Various forms for $f(\varepsilon_G)$, the slip function, were reviewed by Lockett and Kirkpatrick (1975):

Turner (1966) $f(\varepsilon_G) = 1$ (5.1.1.4)

Wallis (1962) $f(\varepsilon_G) = (1-\varepsilon_G)^{n-1}$ (5.1.1.5)
$n=2$ for bubbly flow regime
$n=0$ for churn-turbulent regime

Davidson and Harrison (1966) $f(\varepsilon_G) = 1/(1-\varepsilon_G)$ (5.1.1.6)

Richardson and Zaki (1954) $f(\varepsilon_G) = (1-\varepsilon_G)^{1.39}$ (5.1.1.7)

Lockett and Kirkpatrick (1975) $f(\varepsilon_G) = (1-\varepsilon_G)^{1.39}(1+2.55\varepsilon_G^{3})$ (5.1.1.8)

Marrucci (1965) $f(\varepsilon_G) = (1-\varepsilon_G)/(1-\varepsilon_G^{3/5})$ (5.1.1.9)

Towell et al. (1968) $f(\varepsilon_G) = 1 + 2\varepsilon_G$ (5.1.1.10)

The above slip functions, with the exception of Wallis at $n=0$ and Davidson and Harrison, attempt to describe behavior in the bubbly flow regime. They also share the common feature that the slip velocity approaches the single bubble, terminal rise velocity as the gas holdup tends toward zero.

In the Wallis slip function, when $n>1$, the gas bubbles do not coalesce. Increasing the gas flow adds bubbles which tend to hinder the bubble rise. Rice et al. (1974) found $n=2$ using a surfactant. When $n=1$, the bubble rise velocity is independent of gas holdup. Towell et al. (1968) and Reith et al. (1968) found this to be the case. At $n=0$ the system is in the churn-turbulent regime (e.g. Davidson and Harrison, 1966). Bubble coalescence becomes pronounced. The larger bubbles so formed travel up the column faster, reducing the gas holdup.

Zuber and Finlay (1965) proposed the distribution parameter, C_O, as a correction to the drift flux theory to account for variations in concentration and velocity across the column cross section.

$$C_0 = \langle \varepsilon_G j \rangle / (\langle \varepsilon_G \rangle \langle j \rangle) \qquad (5.1.1.11)$$

where <> is the cross section average quantity. They analytically showed that $1.0 < C_0 < 1.5$ in the bubbly flow and churn-turbulent regimes. In the churn-turbulent regime, they plotted the data of others according to the relation:

$$\langle j_G \rangle / \langle \varepsilon_G \rangle = C_0 \langle j \rangle + \langle j_{GL} \rangle / \langle \varepsilon_G \rangle \qquad (5.1.1.12)$$

with $\langle j_G \rangle / \langle \varepsilon_G \rangle$ on the ordinate and $\langle j \rangle$ on the abscissa. C_0 was found to be a constant < 1.5 for most data sets in this regime.

Substituting eq (5.1.1.1) into the above equation and rearranging gives

$$\varepsilon_G = j_G / (C_0 j + U_{GL}{}^*(1-\varepsilon_G)) \qquad (5.1.1.13)$$

It will be seen below that this equation has been used by several investigators.

Providing verification for the use of C_0, Hills (1974) experimentally examined the radial gas holdup profiles in an air-water system. He found that the gas holdup and velocity were much higher in the column center in the churn-turbulent regime. This maldistribution increased with gas velocity. An examination of Hill's data showed C_0 to be a function of gas velocity although C_0 did not vary significantly.

Hills also concluded that "radial variation of holdup provided the driving force for (liquid) circulation."

Along lines similar to Zuber and Finlay, Nicklin (1962) saw the bubble velocity as composed of three superimposed components: the sum of gas and liquid superficial velocities, j, and the bubble rise velocity, u_B. He developed the following correlation for the slug flow regime,

$$\varepsilon_G = j_G / U_G = j_G / (A(j) + u_B) \qquad (5.1.1.14)$$

where

$A = 1.2$ for two-phase slug flow

$A = 1.783$ for three-phase slug flow

$u_B = 0.35\ (gD)^{1/2}$

"A" is the Zuber and Finlay distribution parameter, C_0. The relationship for u_B is close to the $0.47(gD)^{1/2}$ analytically derived by Davies and Taylor (1950) for very large bubbles, when the effects of surface tension and viscosity are negligible. That $A>1.5$ for three-phase slug flow shows that the solid particles used in Nicklin's study promoted bubble coalescence. It also shows that C_0 can be greater than the 1.5 asserted by Zuber and Finlay.

The form of the above equation is very similar to the rearranged Zuber and Finlay equation (5.1.1.13). By using other relationships for the single bubble rise velocity, the Nicklin relation should be applicable to other flow regimes.

Hills (1976) developed a correlation using the distribution parameter, C_0, applicable when $j_L>30$ cm/s

$$\varepsilon_G = j_G/(u_B+C_0(j)^{0.93}) \qquad (5.1.1.15)$$

where

u_B = single bubble-free rise velocity in water = $0.24\ \mathrm{m\ s^{-1}}$

$C_0 = 1.35$

This relationship is similar to the Nicklin result. However, he used a constant for the single bubble rise velocity, as empirically observed by Calderbank (1961).

While the drift-flux approach has received wide application, other investigators have taken a more empirical approach. Akita and Yoshida (1973) studied four gases and six liquids, encompassing a wide range of physical properties. Using dimensional analysis they fit their data to the correlation:

$$\varepsilon_G/(1-\varepsilon_G)^4 = a\ Bo^{1/8} Ga^{1/12} Fr \qquad (5.1.1.16)$$

where

$a = 0.20$ for nonelectrolytes
$\quad\ \ 0.25$ for electrolytes

The higher value for electrolytes indicates that the bubbly flow regime is maintained to a higher gas holdup in electrolytes than nonelectrolytes. Electrolytes tend to be noncoalescing. The 4th power relationship in the left-hand side denominator was chosen to fit the data better. It does not have the significance of the drift-flux exponent. The low values of gas holdup predicted by this correlation indicate that the churn-turbulent regime was reached at a fairly low gas velocity.

Bach and Pilhofer (1978) studied five liquids in a 10 cm ID by 200 cm tall bubble column. Also encompassing a wide range of liquid physical properties, their empirical correlation is,

$$\varepsilon_G/(1-\varepsilon_G) = 0.115(ReFr^2)^{0.23} \qquad (5.1.1.17)$$

While predicting slightly higher gas holdups than Akita and Yoshida, Bach and Pilhofer used pure, coalescing, organic liquids. When cast in drift-flux terms, the exponent "n" is close to zero confirming that the data was in the churn-turbulent regime.

When noncoalescent liquids are used, it is possible to obtain higher gas holdups and still be in the bubbly flow regime. Kelkar et al. studied various electrolytes (1983a) and alcohols (1983b), which exhibited noncoalescent tendencies. Gas holdup was 25% higher than for an air-water system up to a gas velocity of 10 cm/s. Their electrolyte data was correlated by:

$$\varepsilon_G = 0.475\ j_G^{0.37}\ \mathrm{m\ s^{-1}} \qquad (5.1.1.18)$$

and their alcohol data by:

$$\varepsilon_G = 0.96 j_G^{0.58} C_N^{0.26}/(1 + 2.6\ J_L) \qquad (5.1.1.19)$$

The carbon number effect on gas holdup indicates that low concentrations, 0.5-2.4 wt%, of alcohols tend to stabilize the bubbles.

Hikita and Kikukawa (1973) studied the effect of liquid properties on gas holdup. They initially found surface tension to have a large effect in the aqueous mixtures studied,

$$\varepsilon_G = 4.4 * j_G^{0.47}\ (72/\sigma)^{2/3} (1/\mu)_L^{0.05} \qquad (5.1.1.20)$$

Their considerably higher values indicate that they used noncoalescent liquids.

Hikita et al. (1980) expanded on the earlier work using a larger variety of liquids and examining the effect of gas properties. The work showed a minor effect of gas properties and a much smaller effect of surface tension on gas holdup. It also showed that electrolytes increased gas holdup,

$$\varepsilon_G = 0.672 f (j_G \mu_L/\sigma)^{0.578} (\mu_L g/\rho_L \sigma^3)^{-0.131} (\rho_G/\rho_L)^{0.062}\ (\mu_G/\mu_L)^{0.107} \qquad (5.1.1.21)$$

where

$$f = 10^{0.04141} \text{ when } 0<\text{g-ion/liter}<1$$

$$1.1 \text{ when g-ion/liter}>1$$

Mersmann (1977) used the Akita and Yoshida (1973) data, along with his own, to obtain the following correlation:

$$\varepsilon_G/(1-\varepsilon_G)^4 = 0.14\ j_G Ku^{1/4} Fl^{1/24} (\rho_L/\rho_G)^{1/36} \qquad (5.1.1.22)$$

Godbole et al. (1984) examined gas holdup in non-Newtonian carboxymethyl cellulose solutions. Using a 30.5 cm ID by 3.4 m column they empirically obtained:

$$\varepsilon_G = 0.207 j_G^{0.6} \mu^{-0.19} \qquad (5.1.1.23)$$

The viscosity of a non-Newtonian solution is, by definition, a function of shear rate. The shear rate in a bubble column has been investigated by Nishikawa, Kato, and Hashimoto (1977) and was discussed in the physical property determination section of this report.

5.1.2 Gas-Liquid-Solid Systems

The addition of a solid phase greatly complicates the hydrodynamics of the system. Particles greater than 10 microns tend to settle. Slurry physical properties, such as density and viscosity, then become a function of height. Since liquid properties were shown to play a major role in bubble coalescence (Kelkar, 1983a+b) and hence, gas holdup, solids addition would also be expected to play an important role.

Chern, Fan, and Muroyama (1984) examined gas holdup in a three-phase cocurrent bubble column using 0.3-0.6 cm diameter glass and PVC. They found that adding an empirical correction to Nicklin's work predicted ε_G well for noncoalescing systems:

$$\varepsilon_G = \frac{j_G}{A^* j_T + j_B} \qquad (5.1.2.1)$$

where

$j_T = j/(1-\varepsilon_S)$ = total gas + liquid superficial velocity, once the solid volume is eliminated.

$j_B = 10.16 + 14.88\ (j_G/(1-\varepsilon_S))^{1/2}$ = bubble rise velocity in stagnant liquid.

They also developed an empirical correlation for coalescing systems:

$$\varepsilon_G = 0.098 j_G^{0.7} / j_L^{0.98} \qquad (5.1.2.2)$$

Begovich and Watson (1978) measured gas holdup in an air-water system with added 4.6 mm glass, 6.2 mm alumina or 6.3 mm plexiglass beads in 7.62 cm and 15.2 ID cm columns. They developed the following empirical correlation:

$$\varepsilon_G = 0.048\ j_G^{0.72} d_p^{0.168} D^{-0.125} \qquad (5.1.2.3)$$

It is not surprising that they observed a column diameter effect on gas holdup. Their smallest column was smaller than the 12.7 cm minimum diameter suggested by Akita and Yoshida (1973) as the minimum size to avoid wall effects. The observed increase in gas holdup with particle diameter suggests that smaller particle sizes promote bubble coalescence.

Kara et al. (1982) measured gas holdups in an air-water-(coal or mineral matter) system in a 15.24 cm column. They used the drift-flux model:

$$j_{GL} = u_B \varepsilon_G (1-\varepsilon_G)^n \tag{5.1.2.4}$$

empirically determining the exponent "n" as a function of slurry properties:

$$n = -(1.951 \times 10^{-4} Re_{SL} + 20.624(\varepsilon_S/(\varepsilon_S+\varepsilon_L)) + 56.36 Re_p + 2.607) \tag{5.1.2.5}$$

where,

$Re_{SL} = D j_{SL} \rho_{SL}/\mu_{SL}$
$Re_p = d_p j_p \rho_L/\mu_L$
j_{SL} = slurry superficial velocity, cm s^{-1}
j_p = solid particle terminal settling velocity

Kara found solid particles to promote bubble coalescence and hence the onset of the churn-turbulent regime. This agrees with Nicklin's larger value of C_0 for three-phase systems.

However, solid particle addition does not always promote bubble coalescence. Michelsen and Ostergaard (1970), using glass ballotini in air-water, found bubble breakup to occur in beds of large particles, about 6 mm, at high liquid and low (< 15 cm s^{-1}) gas superficial velocities. In these cases, gas holdup with solids was greater than gas holdup without solids. Viswanathan et al. (1965) also noticed 4 mm diameter glass beads increased gas holdup, while smaller particles promoted bubble coalescence.

Some investigators observed solid particle addition to increase gas holdup while others have found it to decrease gas holdup. When solids addition promotes bubble breakup, the average bubble size is smaller, the bubble rise velocity is reduced, and the gas holdup increases.

Sittig, whose work is described by Kurten and Zehner (1979), studied bubble breakup caused by solid particle addition. He showed that bubble breakup occurs when the inertia forces of the solid particle exceed the bubble surface tension forces.

$$\frac{\pi}{6} \frac{\rho_s}{2} d_s^3 \; u_{SG}^2 > \sigma \; \frac{\pi}{4} d_s^2 \qquad (5.1.2.6)$$

Rearranging the above equation it is seen that bubble breakup can occur when the Weber number is greater than 3:

$$We = \rho_s \; d_s \; u_{SG}{}^2/\sigma \geq 3 \qquad (5.1.2.7)$$

Below the critical Weber number, it is not possible for the solid particles to cause bubble breakup.

For d_s ~ 100 µm iron oxide, a bubble rise velocity >0.65 m s^{-1} is needed for the particle to induce bubble breakup. Thus, over the anticipated range of slurry column operation, bubble breakup by the solids is not expected to take place. In fact, when bubble breakup does not occur, it has been observed that bubble coalescence does, due in part to a viscosity increase. This results in higher bubble rise velocities and correspondingly lower gas holdups in these three-phase systems. When d_s=4 mm, a bubble rise velocity >0.1 m s^{-1} is needed for the particle to induce bubble breakup.

Darton and Harrison (1975) found that the two-phase drift-flux approach modeled the three-phase Michelsen and Ostergaard (1970) data for both flow regimes. In the bubble flow regime,

$$j_{GL} = 18\varepsilon_G \qquad (5.1.2.8)$$

In the churn-turbulent regime they recommended the approach of Zuber and Finlay (1965).

Khang, Schwartz, and Buttke (1982) used the drift-flux approach along with empirical data derived from 5 cm and 15.2 cm ID fluidized beds containing 1 mm cylindrical solid particles. Their best fit to the data was

$$j_{GL} = (1-\varepsilon_G)j_G - \varepsilon_G j_L = \varepsilon_G(22.67\varepsilon_G+10.44) \qquad (5.1.2.9)$$

which can be quadratically solved for ε_G to yield:

$$\varepsilon_G=(-j-10.44+[(j+10.44)^2+90.68j_G]^{1/2})/45.34 \qquad (5.1.2.10)$$

where $j = j_G + j_L$ and all velocities are in cm s^{-1}.

Adlington and Thompson (1965) using 0.3-2.8 mm alumina in white spirit in a 7.6 cm diameter bed and 0.3 mm sand in water in a 25.4 cm diameter bed observed a decrease in gas holdup due to the presence of solids.

Deckwer et al. (1980) studied gas holdup in 4.1 cm and 10 cm ID columns in the bubbly flow regime (1 to 4 cm s^{-1}) using Vestawax, a hydrogenated, Fischer-Tropsch liquid, with up to 16 wt%, <5 micron Al_2O_3 to obtain the following empirical correlation:

$$\varepsilon_G = 0.053j_G^{1.1} \qquad (5.1.2.11)$$

Deckwer used a sintered metal plate. While the high gas holdups obtained indicated foaming, it was possible that a nonfoaming region existed in the lower part of the column. Unfortunately, the experimental setup did not allow for local gas holdup measurements. Kuo et al. (1983), using the same system, showed that the choice of distributor dictated the resulting flow regime for this system. Using a sintered plate, Kuo also experienced a foam region. However, with a larger distributor, no foaming and much lower gas holdups were observed.

Bukur (1985), working in the same Vestawax system as Kuo and as Deckwer, observed that operational procedures could suppress the formation of the undesirable foam region, resulting in gas holdups much closer to the Pilhofer and Bach (1978) correlation discussed in section 5.1.1. Bukur's results are also much closer to this work's results. When operating in the foam region, Bukur obtained gas holdup values slightly in excess of Deckwer's observations. This difference, when operating in the foam region, may have been due to the different methods used in measuring gas holdup.

In view of the above, it is expected that at superficial gas velocities ($j_G > 6$ cm s^{-1}) where a commercial Fischer-Tropsch unit would operate, Deckwer's correlation would predict gas holdups which are too high.

In a subsequent work, Deckwer (1981) indicated that the exponent in the above equation varied from 0.7 to 1.2 in the bubbly flow regime and from 0.4 to 0.7 in the churn-turbulent regime. It is believed that even these predictions are still too high for this system.

Reasonable agreement with the Deckwer correlation was found by Humphreys et al. (1983). They used hexane and octacosane (C_{28}) in a gas velocity range of only 0.4-3.5 cm s^{-1}, in a batch system, with 25 to 45 micron iron oxide particles, to obtain the relation,

$$\varepsilon_G = 0.0694 j_G^{0.976} \qquad (5.1.2.12)$$

It is not surprising that good agreement was obtained. In the bubbly flow regime, most correlations give similar results. Both Deckwer and Humphreys used sintered-metal distributor plates.

Ying et al. (1980) used water/nitrogen and methanol/nitrogen systems in 5 cm and 12.7 cm ID columns. They studied gas holdup both with and without <105 micron or 350-595 micron silicon oxide particles. They found that at low gas velocities, the presence of solids decreased gas holdup. Above 6 cm s^{-1}, the reduction was negligible. They found good agreement to the two-phase Akita and Yoshida (1973) correlation using liquid, not slurry, physical properties.

Koide et al. (1984) used a dimensional analysis approach similar to Akita and Yoshida, extending their work to include the effect of added solids and different diameter vessels in the following gas holdup correlation for the heterogenous (churn-turbulent) flow regime:

$$\varepsilon_G/(1-\varepsilon_G)^4 = AB^{0.918}C^{-0.252}/(1+4.35D^{0.748}E^{0.881}F^{-0.168}) \qquad (5.1.2.13)$$

where

$A = 0.277$ for nonelectrolytes

$= 0.364$ for electrolytes

$B = j_G\mu_L/\sigma_L$

$C = g\mu_L^4/\rho_L\sigma_L^3$

$D = c_S/\rho_S$

$E = (\rho_S-\rho_L)/\rho_L$

$F = D_T j_G \rho_L)/\mu_L$

Koide and coworkers distinguished between the churn-turbulent and transition regime, noting that the effect of solids was less pronounced in the former. Koide et al. were limited to aqueous systems. They also did not try to look at slurry properties. Lastly, their three-phase correlation does not yield their two-phase correlation when solids are not used.

Kato et al. (1973), working with an aqueous sodium sulfite solution in a 12.2 cm column and using four sizes of 2.52 gm cm^{-3} glass spheres ranging from 63 to 177 microns, also found gas holdup decreased both with increasing particle loading and with particle size. It was unexpected, compared to the work of others, for an increase in particle size to reduce gas holdup.

Razumov et al. (1973), working with an air/water/0.9 mm quartz sand system in a 15 cm column, empirically derived the following correlation:

$$\varepsilon_G = 0.02358 j_G + (0.03198 - 0.0135 d_p[cm]^{-0.562}) j_L \qquad (5.1.2.14)$$

While the effect of solids addition was slight, Razumov et al. noticed an increase in gas holdup with solid particle size. The result concurs with the previous discussion on the effect of particle size on gas holdup.

5.2 Experimental

Gas holdup was measured (Method 1), at steady state, by shutting off both the gas and liquid flows and then measuring the settled liquid height. Gas holdup was then determined from the following equation:

$$\varepsilon_g = 1 - H_s/H_e \qquad (5.2.1)$$

where ε_g = gas holdup

H_s = settled slurry height

H_e = expanded slurry height

This was the most reliable method and was always used. A second method (Method 2) was used for part of the runs to measure more localized average gas holdup values between sample ports, instead of column average values. This second method also allowed gas holdup determinations to be obtained without ending or disturbing the run.

Method 2 used manometer tubes filled with the liquid phase. Referring to Figure 5.2.1, the gas holdup was determined from the following equation:

$$\varepsilon_G = 1 - (\frac{H'' - H'}{A} + 1)\ [1 + w_S\ (\frac{P_L}{P_S} - 1)] \qquad (5.2.2)$$

where:

A = distance between manometers

H' = liquid height in upper manometer tube

H'' = liquid height in lower manometer tube

w_s = log average solid weight fraction between the two manometer levels

w_S = exp. [(ln w_{S1} + kn w_{S2})/2]

$P_{L,S}$ =density of liquid, solid

Please refer to Appendix A-1 for a derivation of Equation 5.2.2.

This method was less reliable than the first method because the average weight fraction, W_S, could not be known precisely. Also, any solid or gas entering the manometer tubes affected the measurement, a chronic problem.

A third method (Method 3) was used to overcome the manometer tube contamination problem. A mercury manometer was connected to the two ports according to Figure 5.2.2.

The gas holdup could then be obtained from the following:

$$\varepsilon_G = 1 - \frac{H_{Hg}\rho_{Hg}}{A}\left(\frac{w_S}{\rho_S} + \frac{(1-w_S)}{\rho_L}\right) \tag{5.2.3}$$

where

H_{Hg} = mercury manometer height
ρ_{Hg} = mercury density

Methods 2 and 3 generally gave values within 10% of Method 1. Neither Method 2 nor 3 was able to yield meaningful numbers from the bottommost port when solid settling occurred.

5.3 Results

Gas holdup results are tabulated in Table 5.3.1 for the 12.7 cm cold flow simulator (CFS) and in Table 5.3.2 for the 30.5 cm CFS.

Separate empirical gas holdup correlations were obtained for each of the four solid/liquid pairs studied in the 12.7 cm CFS.

Silicon Oxide/Aqueous (5.3.1)

$$\varepsilon_G/(1-\varepsilon_G)^4 = 0.36\ j_G^{\ 0.96}/d_p^{\ 0.10}/W^{\ 0.27} \qquad R^2 = 0.94$$

Silicon Oxide/Isoparaffin (5.3.2)

$$\varepsilon_G/(1-\varepsilon_G)^4 = 1.26\ j_G^{\ 0.99}/d_p^{\ 0.035} \qquad R^2 = 0.80$$

Iron Oxide/Aqueous (5.3.3)

$$\varepsilon_G/(1-\varepsilon_G)^4 = 1.20\ j_G^{\ 1.02} \qquad R^2 = 0.621$$

Iron Oxide/Isoparaffin (5.3.4)

$$\varepsilon_G/(1-\varepsilon_G)^4 = 1.50\ j_G{}^{0.972}/W^{0.035} \qquad R^2 = 0.812$$

For the 30.5 cm cold flow simulator the eight independent variables in Table 2.1 were analyzed to see what effect they had on gas holdup. In order to efficiently quantify the effects of these variables, a Box-Behnken experimental design was employed.

As the 30.5 cm CFS studies were done after the 12.7 cm ID CFS work, several improvements were incorporated into the gas holdup analysis. A more accurate gas velocity value was determined using a gas orifice meter instead of a rotameter. Also, slurry density and viscosity were used instead of liquid properties. These improvements yielded the following correlation for the 30.5 cm CFS:

$$\varepsilon_G/(1-\varepsilon_G)^4 = 0.483 j_G{}^{1.03}/\rho_{SL}{}^{2.26}\ HS^{0.056} j_L{}^{0.049}$$

$$R^2 = 0.91 \qquad (5.3.5)$$

Where

$\rho_{SL} = \rho_L/(1 - W(1-\rho_L/\rho_S))$
$(\rho_{SL,S,L})$ = Density; slurry, solid, liquid g cm^{-3}
(j_L) = Liquid velocity, ft/sec

For $j_L = 0$ experimental runs, a value of $j_L = 0.0001$ was used to accommodate the correlation.

5.4 Discussion

For both the 12.7 cm and 30.5 cm cold flow simulators, gas holdup was found to be mostly a function of gas velocity. Each correlation has gas velocity varying to the first power in agreement with Akita and Yoshida (1973). Slurry density or weight loading has the second largest effect. There are some differences between the various